Table VI. Bond Angles in the Salicylaldimine Groups and Their E.s.d.'s

Angle	$\angle$, deg.	σ, deg.	Angle	$\angle$, deg.	σ, deg.
O-1–C-1–C-6	123.3	0.8	O-2–C-11–C-16	124.3	1.0
O-1–C-1–C-2	117.1	1.1	O-2–C-11–C-12	116.2	0.9
C-6–C-1–C-2	119.6	1.0	C-16–C-11–C-12	119.5	1.1
C-1–C-2–C-3	118.1	1.2	C-11–C-12–C-13	120.1	1.0
C-2–C-3–C-4	122.8	1.1	C-12–C-13–C-14	120.6	1.2
C-3–C-4–C-5	118.3	1.3	C-13–C-14–C-15	120.6	1.4
C-4–C-5–C-6	120.9	1.3	C-14–C-15–C-16	121.1	1.1
C-5–C-6–C-1	120.1	0.8	C-15–C-16–C-11	118.0	1.0
C-5–C-6–C-7	114.2	1.1	C-15–C-16–C-17	118.0	0.9
C-1–C-6–C-7	125.7	1.1	C-11–C-16–C-17	123.9	1.1
C-6–C-7–N-1	124.0	1.2	C-16–C-17–N-2	127.6	1.0
C-7–N-1–C-8	112.1	1.1	C-17–N-2–C-18	115.8	0.9
N-1–C-8–C-10	104.8	1.1	N-2–C-18–C-20	111.4	1.1
N-1–C-8–C-9	107.6	0.9	N-2–C-18–C-19	109.2	1.1
C-9–C-8–C-10	110.0	1.1	C-19–C-18–C-20	116.0	1.0
C-1–O-1–Cu	128.3	0.7	C-11–O-2–Cu	125.6	0.6
C-7–N-1–Cu	123.1	0.7	C-17–N-2–Cu	123.0	0.7
C-8–N-1–Cu	124.6	0.8	C-18–N-2–Cu	121.0	0.8

Table VII. Coefficients of Least-Squares Plane Equations, $Ax + By + Cz = d$ (x, y, z in Å.)

	A	B	C	d
I Salicylaldimine	0.3999	−0.3191	0.8591	0.7937
Coordination	0.5337	−0.3195	0.7830	0.5917
Isopropyl	0.7232	0.6785	−0.1289	0.0093
II Salicylaldimine	0.7749	0.5357	0.3355	3.4788
Coordination	0.7328	0.5666	0.3766	3.5654
Isopropyl	−0.1434	0.3153	−0.9381	2.3291

The planes defined by the carbon atoms of the isopropyl groups are nearly normal to the planes of the salicylaldimine groups to which they are attached.

Table VIII. Distances from Least-Squares Planes of Salicylaldimine Residues

	d, Å.		d, Å.
C-1	−0.043	C-11	−0.006
C-2	0.011	C-12	−0.014
C-3	0.043	C-13	0.015
C-4	−0.007	C-14	0.001
C-5	−0.032	C-15	0.004
C-6	−0.025	C-16	−0.013
C-7	0.053	C-17	−0.009
N-1[a]	0.115	N-2	0.012
O-1[a]	−0.099	O-2	0.009
Cu[a]	−0.172	Cu[a]	−0.077

[a] Atoms not included in the calculation of the least-squares plane.

Table IX. Intermolecular Distances Less than 3.8 Å.

Atom 1[a]	Atom 2	Distance	Molecule Position
C-15	C-3	3.713	$x + {}^1/_2,\ {}^1/_2 - y,\ \bar{z}$
C-15	C-4	3.754	$x + {}^1/_2,\ {}^1/_2 - y,\ \bar{z}$
C-15	C-20	3.752	$x + {}^1/_2,\ {}^1/_2 - y,\ \bar{z}$
C-16	C-20	3.665	$x + {}^1/_2,\ {}^1/_2 - y,\ \bar{z}$
C-17	C-2	3.749	$x,\ {}^1/_2 - y,\ z - {}^1/_2$
C-18	C-1	3.788	$x,\ {}^1/_2 - y,\ z - {}^1/_2$
C-20	C-5	3.582	$x,\ {}^1/_2 - y,\ z - {}^1/_2$
C-20	C-6	3.512	$x,\ {}^1/_2 - y,\ z - {}^1/_2$
C-20	C-7	3.730	$x,\ {}^1/_2 - y,\ z - {}^1/_2$
O–1	C-5	3.274	${}^1/_2 + x,\ y,\ {}^1/_2 - z$
C-12	C-10	3.577	${}^1/_2 + x,\ y,\ {}^1/_2 - z$

[a] In x, y, z.

In Table IX are listed the intermolecular distances less than 3.8 Å. All these distances appear to be normal.

The Nature of the Chemical Bond in Lithium Hydride and Hydrogen Fluoride

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Abstract: The Hartree–Fock charge distributions for the LiH and HF molecules are examined from the point of view of the forces they exert on the nuclei. The density resulting from each molecular orbital is classified either as binding, nonbinding, or antibinding with respect to the forces it exerts on the nuclei. In addition, whether the bonding in these molecules is primarily ionic or covalent in character is also determined, since these two extremes of bonding exhibit very characteristic features in their density distributions and in the nature of the forces exerted on the nuclei.

Hartree–Fock wave functions have been determined for the LiH and HF molecules.[2,3] A Hartree–Fock wave function yields a one-electron density distribution which is correct to the second order,[4] and thus such a density and its dependent properties can provide a reliable description of a chemical bond. The forces which are exerted on a nucleus in a molecule are determined by the one-electron density distribution, and we choose this property together with the density distribution itself to obtain an understanding of the binding in a molecule. We have previously applied

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(1) A. P. Sloan Research Fellow.

(2) S. L. Kahalas and R. K. Nesbet, *J. Chem. Phys.*, **39**, 529 (1963).

(3) R. K. Nesbet, *ibid.*, **36**, 1518 (1962).

(4) C. W. Kern and M. Karplus, *ibid.*, **40**, 1374 (1964). These authors show that electron-density maps are of great value in the comparison of molecular charge distributions obtained from different wave functions of increasing complexity. This is illustrated for a series of calculations on hydrogen fluoride. They also prove that a *necessary* condition for an exact Hartree–Fock solution is that its expectation values for the forces acting on the nuclei in a diatomic molecule, as determined by the Hellmann–Feynman theorem, be equal.

such an analysis to the LiF molecule.[5] In the present paper we report on LiH and HF. Ionic and covalent bonds exhibit very characteristic features in their density distributions and in the nature of the forces exerted on the nuclei. We illustrate these characteristics through a comparison of the results for the above three molecules.

The force exerted on nucleus A in a diatomic molecule A–B is

$$F_A = \frac{Z_A Z_B}{R^2} - Z_A \int \rho(\bar{r}) \frac{\cos\theta_A}{r_A^2}\, d\tau$$

where R is the internuclear distance, Z_A and Z_B are the nuclear charges, $\rho(\bar{r})$ is the electron density distribution, and $\cos \theta_A/r_A^2$ is the operator which gives the component of the force along the bond. When each molecular orbital is doubly occupied the electron density is

$$\rho(\bar{r}) = 2\sum_i \phi_i^2$$

Since each m.o. makes a separate contribution to the electron density, the total electronic force may be broken up into a sum of orbital contributions. It is convenient to define a quantity f_{iA} for each m.o. as the force exerted on nucleus A by the density in the ith m.o. multiplied by R^2/Z_A. This gives a dimensionless number, and the total force on nucleus A becomes

$$F_A = \frac{Z_A}{R^2}(Z_B - \sum_i f_{iA})$$

The force on each nucleus is zero for large values of R and for the equilibrium internuclear separation, R_e. Thus at these two values of R, $Z_B = \sum_i f_{iA}$ (or $Z_A = \sum_i f_{iB}$ for F_B). For large values of R each f_{iA} value reduces to the orbital occupation number of the atomic orbital with which the ith m.o. correlates. This is a result of the fact that at this limit the charge density on atom B exerts a field at A equal to that obtained from an equivalent number of point charges located at the B nucleus, irrespective of the symmetry of the atomic orbital. Each electron thus effectively screens one unit of nuclear charge and for a molecule which dissociates into neutral atoms, $\sum_i f_{iA} = Z_B$ and F_A becomes zero. For smaller values of R, however, the exact disposition of the charge density in each orbital determines its f_{iA} value. An increase in the f_{iA} value over its value for large R implies that the formation of the molecule has resulted in a transfer of charge density to the region between the nuclei where it exerts a binding force on the nuclei in excess of the simple screening of an equivalent number of nuclear charges. The f_{iA} value may remain unchanged, in which case it is termed nonbinding as it plays the same role in the molecule as it did for large values of R where the density simply screened an equal number of nuclear charges. The f_{iA} value may decrease at R_e, in which case it is termed antibinding.

As explained more fully in part I,[5] each f_i value is the sum of three contributions which are determined by the atomic and overlap populations. The force exerted on nucleus A due to the density situated solely on A is termed an atomic force. This force is zero unless the atomic density on A is polarized, *i.e.*, polarizations induced by s–p or p–d hybridizations. The overlap forces provide separate measures of the binding of both nuclei by the density resulting from the overlap of orbitals situated on A and B. Any inequality in the sharing of the overlap density by the two nuclei is made evident by differences in their overlap forces. The atomic density on B will screen some fraction of the nuclear charge on B from A. Thus the contribution to the force on nucleus A from the density situated solely on B is called the screening force.

An ionic bond resulting from the transfer of one electronic charge between the atoms has the following characteristics in terms of the forces acting on the nuclei. The screening of the cationic nucleus should be decreased by unity and the screening of the anionic nucleus increased by unity corresponding to the transfer of charge from one center to the other. The forces exerted by the overlap density should be ideally zero, or at least small and unequal for the two nuclei, as the transferred charge is centered on the anion as an atomic density and not in the overlap region. This transfer of charge will result in the cationic nucleus experiencing a net electric field of $-1/R^2$. Thus the remaining atomic density on the cation must polarize away from the anion to overcome the net attractive force. The atomic force term for the cation will thus be negative. The anionic nucleus will experience a force of repulsion due to the net positive charge centered on the cation. Thus the atomic density on the anion must be polarized toward the cation (positive atomic force contributions) to achieve electrostatic equilibrium. A covalent bond, on the other hand, is the result of the transfer of charge density from each atom to the region between the nuclei where it is equally shared by both nuclei. Thus for a covalent bond the screening forces exerted on *both* nuclei should be decreased, and by the same amount. The resulting repulsive forces should then be balanced by large and equal overlap forces. Ionic character will be made evident by inequalities in the screening and overlap forces exerted on the two nuclei.

The density distributions for HF and LiH are analyzed in the light of the above definitions to determine the nature of their bonding. Pauling[6] has defined two methods for the determination of per cent ionic character. The one, based on the ratio of the observed dipole moment to the value of eR, gives the following order for increasing ionic character: HF (39%), LiH (77%), LiF (84%). The second definition, based on the difference in the electronegativities of the two atoms, gives the order LiH (26%), HF (59%), LiF (89%). The two estimates for LiH are vastly different. A comparison of the forces and the density distributions for these three molecules should allow one to assign the correct order to this series.

Hydrogen Fluoride

Tables I and II give the orbital breakdown of the forces exerted on the H and F nuclei in HF. $f_{1\sigma H}$ remains unchanged in value from the case of the separated atoms. Even in the molecule the pair of electrons in the 1σ orbital simply screens two units of the

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[5] R. F. W. Bader and W. Henneker, *J. Am. Chem. Soc.*, **87**, 3063 (1965); this paper will be referred to as part I.

[6] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 98.

Table I. Forces on H in HF[a]

			$f_{i\mathrm{H}}$		Contribution		
H a.o.	F a.o.	HF m.o.	Large R	R_e	Atomic	Overlap	Screening
	$1s^2$	1σ	2.000	2.000	0.000	0.000	2.000
	$2s^2$	2σ	2.000	2.248	0.058	0.526	1.664
$1s^1$	$2p_\sigma{}^1$	3σ	1.000	1.908	0.213	0.553	1.142
	$2p_\pi{}^4$	π	4.000	2.895	0.004	0.134	2.757
		Totals	9.000	9.051	0.275	1.213	7.563

[a] To change an f_i value into a force, multiply by $-(Z/R^2)$. The total forces on the H and F nuclei as determined by the wave function used here are -0.0173 and 0.1044 a.u., respectively. A positive force is in the direction of a nuclear repulsion. $R_e = 1.7328$ a.u. The values for the total forces agree with those given in ref. 4.

Table II. Forces on F in HF

			$f_{i\mathrm{F}}$		Contribution		
H a.o.	F a.o.	HF m.o.	Large R	R_e	Atomic	Overlap	Screening
	$1s^2$	1σ	0.000	0.148	0.146	0.002	0.000
	$2s^2$	2σ	0.000	0.833	0.394	0.382	0.057
$1s^1$	$2p_\sigma{}^1$	3σ	1.000	-0.322	-2.476	1.827	0.327
	$2p_\pi{}^4$	π	0.000	0.307	0.187	0.114	0.006
		Totals	1.000	0.966	-1.749	2.325	0.390

F nuclear charge from the H nucleus and therefore exerts no net binding force on the proton. The absence of any overlap or atomic contribution to $f_{1\sigma\mathrm{H}}$ indicates that the 1σ m.o. is essentially a 1s a.o. on F. The small atomic contribution to $f_{1\sigma\mathrm{F}}$ shows that the orbital is slightly polarized toward the H and exerts a small binding force on the F nucleus. The density in the 2σ m.o. exerts a binding force on both the proton and the F nucleus. The increase in $f_{2\sigma\mathrm{H}}$ over the shielding value of 2.00 is seen to arise from a large overlap contribution. The screening of the F nucleus is simultaneously decreased, indicating that charge density has migrated from the F nucleus to the overlap region. Very little of the charge is transferred to the proton as the screening contribution to $f_{2\sigma\mathrm{F}}$ indicates that a field due to only 0.057 unit of charge on the proton is screened from the F nucleus by the density in this orbital. It is interesting to note that the 2σ overlap charge density exerts a greater force per nuclear charge on the proton than on the F nucleus indicating that the charge transferred from F is unequally shared in favor of the proton. The 2σ density remaining on F is strongly polarized toward the proton. An even greater reorganization of the charge density occurs on the formation of the 3σ m.o. The 3σ m.o. correlates with the singly occupied 1s a.o. on H and the $2p_\sigma$ a.o. on F. Thus for the case of the separated atoms $f_{3\sigma\mathrm{H}} = 1.00$ as only one of the F nuclear charges is screened by the single electron in the F $2p_\sigma$ a.o. The value of $f_{3\sigma\mathrm{H}}$ at R_e is almost double this value indicating that it is the reorganization of the charge in the formation of this m.o. which is primarily responsible for the force binding the proton. This same density exerts an antibinding force on the F nucleus; *i.e.*, the negative value of $f_{3\sigma\mathrm{F}}$ indicates that the 3σ density exerts a force on the F nucleus in a direction away from the proton. An examination of the contributions to the $f_{3\sigma}$ values for both nuclei indicates that charge density is transferred from H to F in the formation of this orbital. The screening of the F nucleus is increased from 1.00 to 1.142 and that of the hydrogen nucleus decreased from 1.00 to 0.33. The overlap charge density is very unequally shared as it exerts a force per unit charge on the F nucleus almost four times greater than on the H nucleus. Even the polarizations are in the same direction. The remaining charge on the proton is polarized to exert a force drawing it toward F while the density on F is very strongly polarized away from the H. It is the force due to this large atomic polarization on F which nullifies the overlap contribution to $f_{3\sigma\mathrm{F}}$ and results in the density of the 3σ orbital being antibinding for the F nucleus. At the equilibrium internuclear distance, the density due to the four π electrons originally on F no longer shields an equivalent number of nuclear charges from the proton. This is a result of the fact that the π electron density is concentrated around, rather than along the molecular axis and is *not* due to a large removal of charge from F. There is a small force exerted on the proton by π density which has been transferred to the overlap region. The π electrons are thus antibinding for the proton when the field they exert on the proton in the molecule is compared with the complete shielding of four nuclear charges for large separation. The π density does exert a binding force on the F nucleus. The contributions to $f_{\pi\mathrm{F}}$ indicate that this force originates in an atomic polarization of the π density toward the proton and in the force exerted by the density transferred to the overlap region. The overlap density in the π m.o. is almost equally shared by H and F as the overlap contributions to the f_π values are almost equal for the two nuclei.

The over-all character of the charge distribution in HF can be determined from the totals given in Tables I and II and from a comparison of these figures with those obtained for LiF in part I.[5] The σ electron density and the forces it exerted on the nuclei in LiF were found to possess the characteristics of an ionic bond to a high degree. For large values of R, the electron density in the 1s, 2s, and $2p_\sigma$ atomic orbitals on F screen five units of nuclear charge from the Li nucleus. At R_e, however, the screening contribution of the σ density increased to 6.2. Thus at R_e the Li nucleus experiences a net *negative* field from charge centered on F. This corresponds to the transfer of charge from the Li to the F. This is borne out by the simultaneous decrease in the screening of the Li nucleus from 3.0 to 2.0 showing that the F nucleus experiences a net field due to one positive charge centered at the Li nucleus. This behavior is to be contrasted with that found for HF. The screening of the F nucleus is *decreased* from 5.0 to 4.8 by the rearrangement of the σ density. Thus there is a net *positive* field acting at the proton from the density situated entirely on the F atom. While the proton is deshielded in the formation of HF, this does not occur to as complete an extent as for Li in LiF. A field due to approximately two-thirds of a positive charge is exerted by the hydrogen in HF as opposed to that due to one unit of positive charge by the Li in LiF. Thus less charge is transferred in HF than in LiF and that which is transferred in HF is placed primarily in the overlap region. There are large forces exerted on both the H and F nuclei by the shared electron density in the region between the two nuclei. The overlap density is

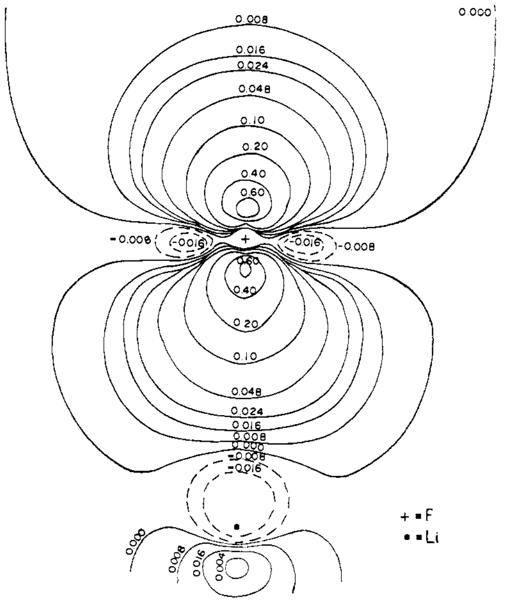

Figure 1. The molecular minus the atomic densities for the σ density distributions for LiF. All the density difference maps are in atomic units and all are drawn to the same scale for comparative purposes. References for the atomic wave functions used to evaluate $\Delta\rho$ are given in part I.[6]

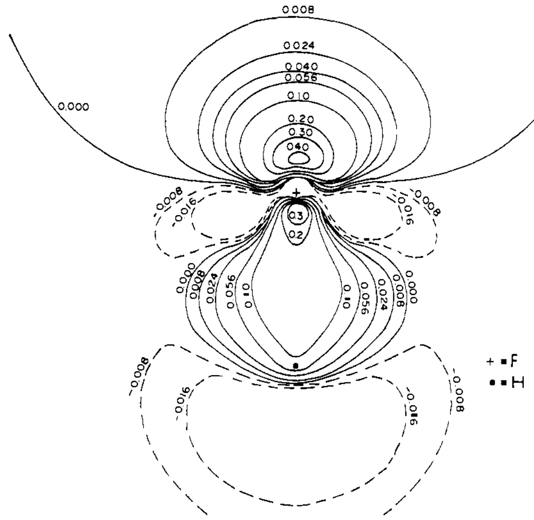

Figure 2. The molecular minus the atomic densities for the σ density distributions for HF.

unequally shared as it exerts twice the force per unit charge on the F nucleus as it does on the proton. However, since over-all the F nucleus is deshielded in the process of forming the molecule, it is the force exerted by the overlap density which is responsible for binding the proton in HF. This is to be contrasted with the binding of the Li nucleus in LiF where the force exerted on Li by the overlap density is close to zero. The Li nucleus is instead bound by the net transfer of charge to the F nucleus itself with a consequent increase in the screening contribution. This is just the behavior which distinguishes an ionic from a covalent bond. Another factor which indicates that HF does not meet the basic requirements of an ionic bond is the sign of the total atomic force term. The cation in an ionic bond must necessarily be polarized away from the anion to achieve electrostatic equilibrium. This behavior was found for Li in LiF in which the atomic density on Li exerts a force on the Li nucleus in a direction away from the F. In HF the density on H is polarized toward F and contributes to the binding of the proton. The atomic polarization on F in HF is also of the wrong direction to achieve electrostatic equilibrium by an ionic mechanism. Instead, reference to Table II shows that the F nucleus is also bound by the forces exerted by the overlap density.

In both HF and LiF the π electron density is polarized into the molecule, and in addition a small amount of π density is transferred to the overlap region. Both effects are slightly more pronounced in LiF than in HF, suggesting that the greater the transfer of charge in the σ density, the larger are the polarization and overlap forces due to the transfer of the π density in the opposite direction.

These basic differences in the electronic makeup of the LiF and HF molecules are borne out in Figures 1 and 2. These are density difference maps for the σ molecular density minus the original σ atomic densities. They thus illustrate the migration of σ charge density which occurs on the formation of the molecule. The F atom density is that for the valence state corresponding to the configuration $1s^22s^22p_\sigma{}^12p_\pi{}^4$. The transfer of charge from Li to F and the accompanying atomic polarizations are clearly indicated in Figure 1. The large increase in charge at F is placed almost symmetrically on each side of the F nucleus and the zero contour line crosses the molecular axis *between* the two nuclei. The density remaining on Li is polarized away from the F giving rise to a region of negative $\Delta\rho$ values between the two nuclei. This is to be contrasted with Figure 2 in which the large accumulation of charge which occurs in the overlap region extends out and encompasses the proton. In HF, electrostatic equilibrium is attained by both nuclei experiencing a net force of attraction by the same portion of the density increase, that portion situated between the two nuclei, the overlap density.

In summary, the forces exerted on the nuclei and the $\Delta\rho$ plot for HF exhibit the essential characteristics of a covalent bond. Each nucleus is descreened and the charge is transferred to the overlap region. The net force binding the nuclei together is exerted by this density which is shared by both nuclei. The ionic character of the bond is evidenced by the unequal force per unit charge exerted by the overlap density (the field exerted at the F nucleus is twice that exerted on the proton) and by the unequal removal of charge from the two atoms in the formation of the molecular density. The HF molecule is therefore a covalent bond with ionic character, rather than *vice versa*. Figure 3 is a density difference map for the total HF molecular density minus the atomic densities. It is to be compared with Figure 2 of part I.

Figure 4 is a plot of the density due to a single electron in a F^- 2p orbital. This plot is strikingly similar to the positive $\Delta\rho$ contours centered on F in the LiF plot. Because of this similarity it is clear that the formation of the bond in LiF corresponds to the transfer of one electron from Li to F to fill the vacant $2p_\sigma$ orbital on F. The $\Delta\rho$ values in HF on the side of F removed from H are again quite similar, in shape at

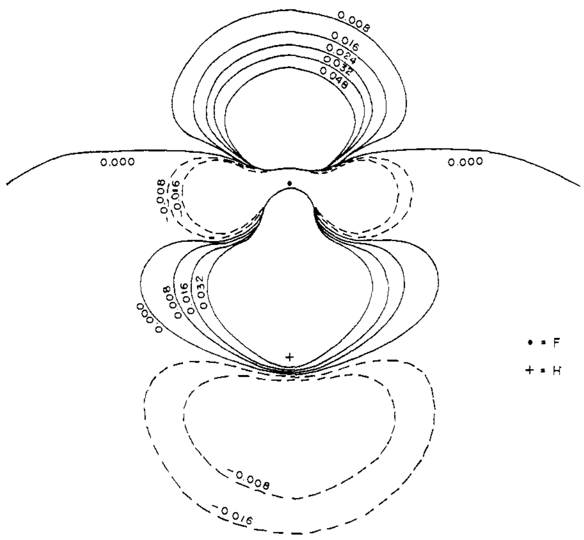

Figure 3. The molecular minus the atomic densities for the total electron density distribution in HF.

least, to those of the singly occupied 2p F^- orbital. The contours on the H side of F are, however, distorted owing to the overlap with the H orbital. Thus the vacant $2p_\sigma$ orbital is also partially filled in the formation of HF and the bond from F is primarily of p character. This explains the large increase in density on each side of the F nucleus. A p orbital concentrates density on both sides of the nucleus it is centered on. This is clearly occurring in HF. Kern and Karplus[4] have previously noted that the formation of the bond in HF results in a concentration of charge not only in the bonding region but also behind the F nucleus.

Lithium Hydride

Tables III and IV give a breakdown of the forces exerted on the nuclei in LiH. The 1σ orbital is primarily a polarized 1s orbital on Li. The polarization exerts a force on the Li away from the H. The same 1σ density is essentially nonbinding for the proton as it screens approximately two units of positive charge of the Li nucleus from the proton. The 2σ density is binding for the Li nucleus. The same density is antibinding for the proton when compared with the screening effect for large R. However, the calculation does not predict a zero force for either nucleus, and the deficit in the $f_{2\sigma H}$ value of $\sim$0.1 unit is almost equal to the total difference between the required value of 3 and the sum of the f_{iH} values. The $f_{2\sigma}$ orbital is in reality probably very slightly binding to make up for the slight decrease in screening found in the 1σ m.o.[7] A large amount of charge is removed from the Li nucleus as the screening contribution to $f_{2\sigma H}$ is reduced to approximately one-quarter. However, unlike the ionic bond in LiF, this density is not transferred to the more electronegative nucleus (the proton in this case). Rather, the screening of the proton is also decreased, to a lesser extent, and the density is accumulated in the overlap region. The overlap density exerts almost equal forces on both nuclei drawing them together. This behavior is characteristic of the covalent bond. However, the atomic polarizations on the Li and H nuclei are in the directions required for an ionic bond, the Li polarized out and the H polarized toward the Li. These polarizations are in the same direction as those found in LiF and opposite to those for HF. The deshielding of the Li nucleus in LiH is less than that found for Li in LiF but greater than that for the proton in HF.

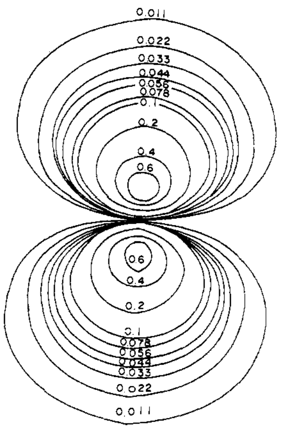

Figure 4. The electron density distribution for a single electron in a fluoride 2p a.o. The density distribution for a fluorine a.o. is very similar to the above. The contours with values greater than 0.1 a.u. are slightly more contracted in F^- than in F and *vice versa* for contours greater than this amount.

Table III. Forces on Li in LiH[a]

H	Li	LiH	f_{iLi} Large R	f_{iLi} R	Contribution Atomic	Contribution Overlap	Contribution Screening
	$1s^2$	1σ	0.00	−0.257	−0.325	0.066	0.002
$1s^1$	$2s^1$	2σ	1.00	+1.560	−0.010	0.730	0.840
		Total	1.00	1.303	−0.335	0.796	0.842

[a] The total forces on the Li and H nuclei calculated for the wave function used here are −0.0995 and +0.0119 a.u., respectively. R_e = 3.02 a.u.

Table IV. Forces on H in LiH

H	Li	LiH	f_{iH} Large R	f_{iH} R_e	Contribution Atomic	Contribution Overlap	Contribution Screening
	$1s^2$	1σ	2.00	1.993	0.002	0.028	1.963
$1s^1$	$2s^1$	2σ	1.00	.898	0.062	0.589	0.247
		Total	3.00	2.891	0.064	0.617	2.210

Pauling's[6] ordering of the relative ionic character in these molecules based on the electronegativity differences, HF > LiH, is reflected in the almost equal overlap forces on the Li and H nuclei as opposed to the factor of two for these forces in HF. However, the ordering based on the observed dipole moment LiH > HF is reflected in the correct signs for the atomic polarizations in LiH and the opposite signs for those in HF and in the greater deshielding of the Li in LiH than of the proton in HF. In addition, the overlap forces in HF, while not equal, are greater than those found in LiH. Reference to Figure 5, a plot of the molecular density minus the atomic density, helps to explain the intermediate behavior of LiH. First, the $\Delta\rho$ contours for LiH have the same general character-

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(7) The absolute values for the forces calculated for LiH are as accurate as those for LiF and HF but the large value of R_e for LiH magnifies the small remaining error in the determination of the f_i values.

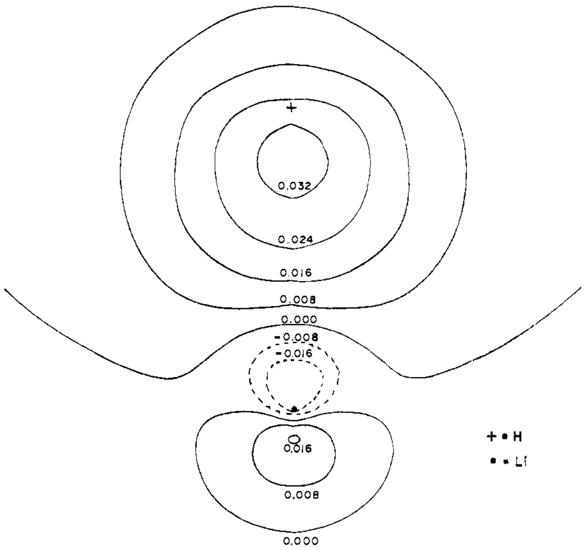

Figure 5. The molecular minus the atomic densities for the total density distribution in LiH.

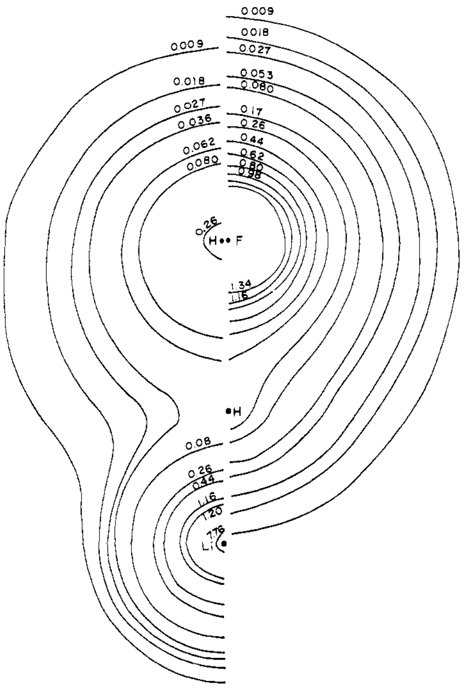

Figure 6. The total molecular electron density distributions for LiH and HF.

istics as those for LiF, and the contours centered on Li are strikingly similar to those shown for Li in LiF (Figure 1). The polarization characteristic of an ionic bond found on the Li in LiH results in a region of negative $\Delta\rho$ values between the two nuclei. Thus the increases in density in LiH are divided into two distinct regions, similar to those found for LiF. The ionic character of the bond is also evidenced by the large diameter of the zero contour line which encompasses only the proton (a large transfer of charge to the more electronegative end of the molecule). There is no single contour line of positive $\Delta\rho$ enveloping both nuclei, corresponding to a shared density as in HF. However, the distribution of the charge transferred to the vicinity of the proton does not resemble that transferred to the F in LiF. Unlike the almost symmetrical $\Delta\rho$ increases around F in LiF, the transferred density in LiH is accumulated on the Li side of the proton. This unsymmetrical distribution of the charge is a result of the fact that it is the charge transferred due to the overlap of the orbitals on the two centers. It is not an increase in the atomic population as it is for F in LiF. The surprising fact emerges that the density transferred owing to the overlap of a.o.'s can be disposed in a manner characteristic of an ionic bond. Thus the chemistry of LiH is characteristic of ionic behavior even though the bonding originates in the forces exerted by the overlap density. Figure 6 illustrates the total molecular density distributions for LiH and HF. The first contour to envelope both nuclei in LiH has a value between 0.06 and 0.04 a.u. (Notice that the contours on H are displaced toward Li.) All the contours of higher density are closed separately around each nucleus. The first contour to encompass both nuclei in LiF also has a low value and lies between 0.02 and 0.09 a.u. Thus the major portion of the density is centered on the nuclei in both these molecules. In HF, on the other hand, the contour of 0.25 a.u. already encompasses both nuclei indicating a greater sharing of the charge density. Figure 6 again emphasizes the more ionic character of the bond in LiH compared to that in HF.

The polarization of the density which remains on Li in LiH and LiF and which is so clearly illustrated in Figures 1 and 5 provides a striking illustration of the large amount of charge which is transferred in the formation of these molecules. The force exerted on the Li nucleus by this transferred charge is so great that the Li nucleus can reach electrostatic equilibrium only by having its remaining density polarize away from the H and F nuclei. This is the origin of the negative $\Delta\rho$ region between the nuclei which is so characteristic of an ionic bond. The fact that the proton in HF is able to attain electrostatic equilibrium with a positive atomic force attests to the smaller amount of charge which is transferred in the formation of this molecule. That the LiH bond is less ionic than the bond in LiF is shown by the large asymmetry in the charge transferred to the H and by the near equality of the electric fields exerted on the nuclei by this overlap charge. In addition, the transfer of charge is less complete in LiH than in LiF. Thus the order of increasing ionic character as determined by the analysis of the molecular charge distributions is HF < LiH < LiF.

Electronegativity is a measure of the ability of an atom to attract electrons to itself. Thus the ionic character of LiH will be underestimated by electronegativity differences. For while the density transferred in the formation of LiH is not placed solely on the proton, as would be required by a high electronegativity, it is still disposed in a manner characteristic of an ionic rather than a covalent bond. The results of this investigation offer no reason as to why the transferred density should be ionic in character for an alkali hydride. However, the density distribution for LiH which correctly predicts this experimental fact was determined by quantum mechanics.